scale. I cannot speak with exactness, as this part of the spectrum requires remapping.

I have evidence that the prominence was a very fine one.

The instrument employed is the solar spectroscope, the funds for the construction of which were supplied by the Government-Grant Committee. It is to be regretted that its construction has been so long delayed.

I have &c.,

J. NORMAN LOCKYER.

The Secretary of the Royal Society.

IX. "On a New Series of Chemical Reactions produced by Light."
By John Tyndall, LL.D., F.R.S., &c. Received October 24,
1868.

I ask permission of the Royal Society to draw the attention of chemists to a form or method of experiment which, though obvious, is, I am informed, unknown, and which, I doubt not, will in their hands become a new experimental power. It consists in subjecting the vapours of volatile liquids to the action of concentrated sunlight, or to the concentrated beam of the electric light.

Action of the Electric Light.

A glass tube 2.8 feet long and of 2.5 inches internal diameter, frequently employed in my researches on radiant heat, was supported horizontally. At one end of it was placed an electric lamp, the height and position of both being so arranged that the axis of the glass tube and that of the parallel beam issuing from the lamp were coincident. The tube in the first experiments was closed by plates of rock-salt, and subsequently by plates of glass.

As on former occasions, for the sake of distinction, I will call this tube the experimental tube.

The experimental tube was connected with an air-pump, and also with a series of drying and other tubes used for the purification of the air.

A number of test-tubes (I suppose I have used fifty of them in all) were converted into Woulfe's flasks. Each of them was stopped by a cork through which passed two glass tubes: one of these tubes (a) ended immediately below the cork, while the other (b) descended to the bottom of the flask, being drawn out at its lower end to an orifice about 0.03 of an inch in diameter. It was found necessary to coat the cork carefully with cement.

The little flask thus formed was partially filled with the liquid whose vapour was to be examined; it was then introduced into the path of the purified current of air.

The experimental tube being exhausted, and the cock which cut off the supply of purified air being cautiously turned on, the air entered the flask

through the tube b, and escaped by the small orifice at the lower end of b into the liquid. Through this it bubbled, loading itself with vapour, after which the mixed air and vapour, passing from the flask by the tube a, entered the experimental tube, where they were subjected to the action of light.

The power of the electric beam to reveal the existence of anything within the experimental tube, or the impurities of the tube itself, is extraordinary. When the experiment is made in a darkened room, a tube which in ordinary daylight appears absolutely clean is often shown by the present mode of examination to be exceedingly filthy.

The following are some of the results obtained with this arrangement:—

Nitrite of amyl (boiling-point 91° to 96° C.).—The vapour of this liquid was in the first instance permitted to enter the experimental tube while the beam from the electric lamp was passing through it. Curious clouds were observed to form near the place of entry, which were afterwards whirled through the tube.

The tube being again exhausted, the mixed air and vapour were allowed to enter it in the dark. The slightly convergent beam of the electric light was then sent through the tube from end to end. For a moment the tube was optically empty, nothing whatever was seen within it; but before a second had elapsed a shower of liquid spherules was precipitated on the beam, thus generating a cloud within the tube. This cloud became denser as the light continued to act, showing at some places a vivid iridescence.

The beam of the electric lamp was now converged so as to form within the tube, between its end and the focus, a cone of rays about eight inches long. The tube was cleansed and again filled in darkness. When the light was sent through it, the precipitation upon the beam was so rapid and intense that the cone, which a moment before was invisible, flashed suddenly forth like a solid luminous spear.

The effect was the same when the air and vapour were allowed to enter the tube in diffuse daylight. The cloud, however, which shone with such extraordinary radiance under the electric beam, was invisible in the ordinary light of the laboratory.

The quantity of mixed air and vapour within the experimental tube could of course be regulated at pleasure. The rapidity of the action diminished with the attenuation of the vapour. When, for example, the mercurial column associated with the experimental tube was depressed only five inches, the action was not nearly so rapid as when the tube was full. In such cases, however, it was exceedingly interesting to observe, after some seconds of waiting, a thin streamer of delicate bluish-white cloud slowly forming along the axis of the tube, and finally swelling so as to fill it.

When dry oxygen was employed to carry in the vapour, the effect was the same as that obtained with air.

When dry hydrogen was used as a vehicle, the effect was also the same.

The effect, therefore, is not due to any interaction between the vapour of the nitrite and its vehicle.

This was further demonstrated by the deportment of the vapour itself. When it was permitted to enter the experimental tube unmixed with air or any other gas, the effect was substantially the same. Hence the seat of the observed action is the vapour itself.

With reference to the air and the glass of the experimental tube, the beam employed in these experiments was perfectly cold. It had been sifted by passing it through a solution of alum, and through the thick double-convex lens of the lamp. When the unsifted beam of the lamp was employed, the effect was still the same; the obscure calorific rays did not appear to interfere with the result.

I have taken no means to determine strictly the character of the action here described, my object being simply to point out to chemists a method of experiment which reveals a new and beautiful series of reactions; to them I leave the examination of the products of decomposition. The molecule of the nitrite of amyl is shaken asunder by certain specific waves of the electric beam, forming nitric oxide and other products, of which the nitrate of amyl is probably one. The brown fumes of nitrous acid were seen to mingle with the cloud within the experimental tube.

The nitrate of amyl, being less volatile than the nitrite, could not maintain itself in the condition of vapour, but would be precipitated in liquid spherules along the track of the beam.

In the anterior portions of the tube a sifting action of the vapour occurs, which diminishes the chemical action in the posterior portions. In some experiments the precipitated cloud only extended halfway down the tube. When, under these circumstances, the lamp was shifted so as to send the beam through the other end of the tube, precipitation occurred there also.

Action of Sunlight.

The solar light also effects the decomposition of the nitrite-of-amyl vapour. On the 10th of October I partially darkened a small room in the Royal Institution, into which the sun shone, permitting the light to enter through an open portion of the window-shutter. In the track of the beam was placed a large plano-convex lens, which formed a fine convergent cone in the dust of the room behind it. The experimental tube was filled in the laboratory, covered with a black cloth, and carried into the partially darkened room. On thrusting one end of the tube into the cone of rays behind the lens, precipitation within the cone was copious and immediate. The vapour at the distant end of the tube was in part shielded by that in front, and

was also more feebly acted on through the divergence of the rays. On reversing the tube, a second and similar cone was precipitated.

Physical considerations.

I sought to determine the particular portion of the white beam which produced the foregoing effects. When, previous to entering the experimental tube, the beam was caused to pass through a red glass, the effect was greatly weakened, but not extinguished. This was also the case with various samples of yellow glass. A blue glass being introduced, before the removal of the yellow or the red, on taking the latter away augmented precipitation occurred along the track of the blue beam. Hence, in this case, the more refrangible rays are the most chemically active.

The colour of the liquid nitrite of amyl indicates that this must be the case; it is a feeble but distinct yellow: in other words, the yellow portion of the beam is most freely transmitted. It is not, however, the transmitted portion of any beam which produces chemical action, but the absorbed portion. Blue, as the complementary colour to yellow, is here absorbed, and hence the more energetic action of the blue rays. This reasoning, however, assumes that the same rays are absorbed by the liquid and its vapour.

A solution of the yellow chromate of potash, the colour of which may be made almost, if not altogether, identical with that of the liquid nitrite of amyl, was found far more effective in stopping the chemical rays than either the red or the yellow glass. But of all substances the nitrite itself is most potent in arresting the rays which act upon its vapour. A layer one-eighth of an inch in thickness, which scarcely perceptibly affected the luminous intensity, sufficed to absorb the entire chemical energy of the concentrated beam of the electric light.

The close relation subsisting between a liquid and its vapour, as regards their action upon radiant heat, has been already amply demonstrated *. As regards the nitrite of amyl, this relation is more specific than in the cases hitherto adduced; for here the special constituent of the beam which provokes the decomposition of the vapour is shown to be arrested by the liquid.

A question of extreme importance in molecular physics here arises:—What is the real mechanism of this absorption, and where is its seat †?

I figure, as others do, a molecule as a group of atoms, held together by their mutual forces, but still capable of motion among themselves. The vapour of the nitrite of amyl is to be regarded as an assemblage of such molecules. The question now before us is this:—In the act of absorption, is it the molecules that are effective, or is it their constituent

^{*} Phil. Trans. 1864.

[†] My attention was very forcibly directed to this subject some years ago by a conversation with my excellent friend Professor Clausius.

atoms? Is the *vis viva* of the intercepted waves transferred to the molecule as a whole, or to its constituent parts?

The molecule, as a whole, can only vibrate in virtue of the forces exerted between it and its neighbour molecules. The intensity of these forces, and consequently the rate of vibration, would, in this case, be a function of the distance between the molecules. Now the identical absorption of the liquid and of the vaporous nitrite of amyl indicates an identical vibrating period on the part of liquid and vapour, and this, to my mind, amounts to an experimental demonstration that the absorption occurs in the main within the molecule. For it can hardly be supposed, if the absorption were the act of the molecule as a whole, that it could continue to affect waves of the same period after the substance had passed from the vaporous to the liquid state.

In point of fact the decomposition of the nitrite of amyl is itself to some extent an illustration of this internal molecular absorption; for were the absorption the act of the molecule as a whole, the *relative* motions of its constituent atoms would remain unchanged, and there would be no mechanical cause for their separation. It is probably the synchronism of the vibrations of one portion of the molecule with the incident waves which enables the amplitude of those vibrations to augment until the chain which binds the parts of the molecule together is snapped asunder.

The liquid nitrite of amyl is probably also decomposed by light; but the reaction, if it exists, is incomparably less rapid and distinct than that of the vapour. Nitrite of amyl has been subjected to the concentrated solar rays until it boiled, and it has been permitted to continue boiling for a considerable time, without any distinctly apparent change occurring in the liquid *.

I anticipate wide, if not entire, generality for the fact that a liquid and its vapour absorb the same rays. A cell of liquid chlorine now preparing for me will, I imagine, deprive light more effectually of its power of causing chlorine and hydrogen to combine than any other filter of the luminous rays. The rays which give chlorine its colour have nothing to do with this combination, those that are absorbed by the chlorine being the really effective rays. A highly sensitive bulb containing chlorine and hydrogen in the exact proportions necessary for the formation of hydrochloric acid was placed at one end of the experimental tube, the beam of the electric lamp being sent through it from the other. The bulb did not explode when the tube was filled with chlorine, while the explosion was violent and immediate when the tube was filled with air. I anticipate for the liquid chlorine an action similar to but still more energetic than that exhibited by the gas. If this should prove to be the case, it will favour the view that

^{*} On the 21st of October, Mr. Ernest Chapman mentioned to me in conversation that he once exposed nitrite-of-amyl vapour to the action of light. With what result I do not know.

chlorine itself is molecular and not monatomic. Other cases of this kind I hope, at no distant day, to bring before the Royal Society.

Production of Sky-blue by the decomposition of Nitrite of Amyl.

When the quantity of nitrite vapour is considerable, and the light intense, the chemical action is exceedingly rapid, the particles precipitated being so large as to whiten the luminous beam. Not so, however, when a well-mixed and highly attenuated vapour fills the experimental tube. The effect now to be described was obtained in the greatest perfection when the vapour of the nitrite was derived from a residue of the moisture of its liquid, which had been accidentally introduced into the passage through which the dry air flowed into the experimental tube.

In this case the electric beam traversed the tube for several seconds before any action was visible. Decomposition then visibly commenced, and advanced slowly. The particles first precipitated were too small to be distinguished by an eye-glass; and, when the light was very strong, the cloud appeared of a milky blue. When, on the contrary, the intensity was moderate, the blue was pure and deep. In Brücke's important experiments on the blue of the sky and the morning and evening red, pure mastic is dissolved in alcohol, and then dropped into water well stirred. When the proportion of mastic to alcohol is correct, the resin is precipitated so finely as to elude the highest microscopic power. By reflected light, such a medium appears bluish, by transmitted light yellowish, which latter colour, by augmenting the quantity of the precipitate, can be caused to pass into orange or red.

But the development of colour in the attenuated nitrite-of-amyl vapour, though admitting of the same explanation, is doubtless more similar to what takes place in our atmosphere. The blue, moreover, is purer and more sky-like than that obtained from Brücke's turbid medium. There could scarcely be a more impressive illustration of Newton's mode of regarding the generation of the colour of the firmament than that here exhibited; for never, even in the skies of the Alps, have I seen a richer or a purer blue than that attainable by a suitable disposition of the light falling upon the precipitated vapour. May not the aqueous vapour of our atmosphere act in a similar manner? and may we not fairly refer to liquid particles of infinitesimal size the hues observed by Principal Forbes over the safety-valve of a locomotive, and so skilfully connected by him with the colours of the sky?

In exhausting the tube containing the mixed air and nitrite-of-amyl vapour, it was difficult to avoid explosions under the pistons of the air-pump, similar to those which I have already described as occurring with the vapours of bisulphide of carbon and other substances. Though the quantity of vapour present in these cases must have been infinitesimal, its explosion was sufficient to destroy the valves of the pump.

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Iodide of Allyl (boiling-point 101° C.).—Among the liquids hitherto subjected to the concentrated electric light, iodide of allyl, in point of rapidity and intensity of action, comes next to the nitrite of amyl. With the iodide of allyl I have employed both oxygen and hydrogen, as well as air, as a vehicle, and found the effect in all cases substantially the same. The cloud column here was exquisitely beautiful, but its forms were different from those of the nitrite of amyl. The whole column revolved round the axis of the decomposing beam; it was nipped at certain places like an hour-glass, and round the two bells of the glass delicate cloud-filaments twisted themselves in spirals. It also folded itself into convolutions resembling those of shells. In certain conditions of the atmosphere in the Alps I have often observed clouds of a special pearly lustre; when hydrogen was made the vehicle of the iodide-of-allyl vapour a similar lustre was most exquisitely shown. With a suitable disposition of the light, the purple hue of iodine-vapour came out very strongly in the tube.

The remark already made as to the bearing of the decomposition of nitrite of amyl by light on the question of molecular absorption applies here also; for were the absorption the work of the molecule as a whole, the iodine would not be dislodged from the allyl with which it is combined. The non-synchronism of iodine with the waves of obscure heat is illustrated by its marvellous transparency to such heat. May not its synchronism with the waves of light in the present instance be the cause of its divorce from the allyl? Further experiments on this point are in preparation.

Iodide of Isopropyl.—The action of light upon the vapour of this liquid is at first more languid than upon iodide of allyl; indeed many beautiful reactions may be overlooked in consequence of this languor at the commencement. After some minutes' exposure, however, clouds begin to form, which grow in density and in beauty as the light continues to act. In every experiment hitherto made with this substance the column of cloud which filled the experimental tube was divided into two distinct parts near the middle of the tube. In one experiment a globe of cloud formed at the centre, from which, right and left, issued an axis which united the globe with the two adjacent cylinders. Both globe and cylinders were animated by a common motion of rotation. As the action continued, paroxysms of motion were manifested; the various parts of the cloud would rush through each other with sudden violence. During these motions beautiful and grotesque cloud-forms were developed. some places the nebulous mass would become ribbed so as to resemble the graining of wood; a longitudinal motion would at times generate in it a series of curved transverse bands, the retarding influence of the sides of the tube causing an appearance resembling, on a small scale, the dirt-bands of the Mer de Glace. In the anterior portion of the tube those sudden commotions were most intense; here buds of cloud would sprout forth, and grow in a few seconds into perfect flewer-like forms. The most curious appearance that I noticed was that of a cloud resembling a serpent's head: it grew rapidly; a mouth was formed, and from the mouth a cord of cloud resembling a tongue was rapidly discharged. The cloud of iodide of isopropyl had a character of its own, and differed materially from all others that I had seen. A gorgeous mauve colour was developed in the last twelve inches of the tube; the vapour of iodine was present, and it may have been the sky-blue produced by the precipitated particles which, mingling with the purple of the iodine, produced this splendid mauve. As in all other cases here adduced, the effects were proved to be due to the light; they never occurred in darkness.

I should like to guard myself against saying more than the facts warrant regarding the chemical effects produced by light in the following three substances; but the physical appearances are so exceedingly singular that I do not hesitate to describe them.

Hydrobromic Acid.—The aqueous solution of this acid was placed in a small Woulfe's flask, and carried into the experimental tube by a current of air.

The tube being filled with the mixture of acid, aqueous vapour, and air, the beam was sent through it, the lens at the same time being so placed as to produce a cone of very intense light. Two minutes elapsed before anything was visible; but at the end of this time a faint bluish cloud appeared to hang itself on the most concentrated portion of the beam.

Soon afterwards a second cloud was formed five inches further down the experimental tube. Both clouds were united by a slender cord of cloud of the same bluish tint as themselves.

As the action of the light continued, the first cloud gradually resolved itself into a series of parallel disks of exquisite delicacy; the disks rotated round an axis perpendicular to their surfaces, and finally they blended together to produce a screw surface with an inclined generatrix. This surface gradually changed into a filmy funnel, from the end of which the "cord" extended to the cloud in advance. This also underwent modification. It resolved itself into a series of strata resembling those of the electric discharge. After a little time, and through changes which it was difficult to follow, both clouds presented the appearance of a series of concentric funnels set one within the other, the interior ones being seen through the spectral walls of the outer ones; those of the distant cloud resembled claretglasses in shape. As many as six funnels were thus concentrically set together, the two series being united by the delicate cord of cloud already referred to. Other cords and slender tubes were afterwards formed, and they coiled themselves in spirals around and along the funnels.

Rendering the light along the connecting-cord more intense, it diminished in thickness and became whiter; this was a consequence of the enlarge-

ment of its particles. The cord finally disappeared, while the funnels melted into two ghost-like films, shaped like parasols. The films were barely visible, being of an exceedingly delicate blue tint; they seemed woven of blue air. To compare them with cobweb or with gauze would be to liken them to something infinitely grosser than themselves.

In a second trial the result was very much the same. A cloud which soon assumed the parasol shape was formed in front, and five inches lower down another cloud was formed, in which the funnels already referred to were considerably sharpened. It was connected as before by a filament with the cloud in front, and it ended in a spear-point which extended 12 inches further down the tube.

After many changes, the film in front assumed the shape of a bell, to the convex surface of which a hollow cylinder about 2 inches long attached itself. After some time this cylinder broke away from the bell and formed itself into an iridescent ring, which, without apparent connexion with anything else, rotated on its axis in the middle of the tube. The inner diameter of this ring was nearly an inch in length, and its outer diameter nearly an inch and a half.

The whole cloud composed of these heterogeneous parts was animated throughout by a motion of rotation. The rapidity of the rotation could be augmented by intensifying the beam. The disks, funnels, strata, and convolutions of the cloud exhibited at times diffraction colours, which changed colour with every motion of the observer's eye.

Moisture appeared to be favourable to the production of these appearances; and it hence became a question how far they were really produced by the light: hydrobromic acid, even from its solution, fumes when it comes into contact with the aqueous vapour of the air; its residence in water does not appear to satisfy its appetite for the liquid. The same effect, as everybody knows, is observed in the solution of hydrochloric acid. Might not, then, those wonderfully shaped clouds be produced by an action of this kind, the presence of the light being an unnecessary accident?

The hydrobromic acid was permitted to enter the experimental tube and remain in diffuse daylight for five minutes. On darkening the room and sending the electric beam through it, the tube was optically empty. Two minutes' action of the light caused the clouds to appear, and they afterwards went through the same variety of changes as before.

No matter how long the hydrobromic acid was allowed to remain in the tube, no action occurred until the luminous beam was brought into play. The tube filled with the mixture of air, aqueous vapour, and hydrobromic acid was permitted to remain for fifteen minutes in the dark. On sending the beam through the tube it was found optically empty; but two minutes' action of the light developed the clouds as before.

Permitting the beam to pass through a layer of water before entering

the experimental tube, no diminution of its chemical energy was observed. Permitting it to pass through a solution of hydrobromic acid, of the same thickness, the chemical energy of the beam was wholly destroyed. This shows that the vibrations of the dissolved acid are synchronous with those of the gaseous acid, and is a new proof that the constituent atoms of the molecule, and not the molecule itself, is the seat of the absorption.

Hydrochloric Acid.—The aqueous solution of this acid was also employed and treated like the solution of hydrobromic acid. I intend to invoke the aid of an artistic friend in an effort to reproduce the effects observed during the decomposition, if such it be, of hydrochloric acid by But artistic skill must, I fear, fail to convey a notion of them. cloud was of slow growth, requiring 15 or 20 minutes for its full development. It was then divided into four or five sections, every adjacent two of which were united by a slender axial cord. Each of these sections possessed an exceedingly complex and ornate structure, exhibiting ribs, spears. funnels, leaves, involved scrolls, and iridescent fleurs-de-lis. Still the structure of the cloud from beginning to end was perfectly symmetrical; it was a cloud of revolution, its corresponding points being at equal distances from the axis of the beam. There are many points of resemblance between the clouds of hydrochloric and hydrobromic acid, and both are perfectly distinct from anything obtainable from the substances previously mentioned; in fact every liquid appears to have its own special cloud, varying only within narrow limits from a normal type. The formation of the cloud depends rather upon its own inherent forces than upon the environment. It is true that, by warming or chilling the experimental tube at certain points, extraordinary flexures and whirlwinds may be produced; but with a perfectly constant condition of tube, specific differences of cloud-structure are revealed, the peculiarity of each substance stamping itself apparently upon the precipitated vapour derived from its decomposition.

When the beam before entering the experimental tube was sent through a layer of the aqueous acid, thirteen minutes' exposure produced no action. A layer of water being substituted for the layer of acid, one minute's exposure sufficed to set up the decomposition.

Hydriodic Acid.—The aqueous solution of this acid was also employed. On first subjecting it to the action of light no visible effect was produced; but subsequent trials developed a very extraordinary one. A family resemblance pervades the nebulæ of hydriodic, hydrobromic, and hydrochloric acids. In all three cases, for example, the action commenced by the formation of two small clouds united by a cord; it was very slow, and the growth of the cloud in density and beauty very gradual. The most vivid green and crimson that I have yet observed were exhibited by this substance in the earlier stages of the action. The de-

velopment of the cloud was like that of an organism, from a more or less formless mass at the commencement, to a structure of marvellous complexity. I have seen nothing so astonishing as the effect obtained, on the 28th of October, with hydriodic acid. The cloud extended for about 18 inches along the tube, and gradually shifted its position from the end nearest the lamp to the most distant end. The portion quitted by the cloud proper was filled by an amorphous haze, the decomposition which was progressing lower down being here apparently complete. A spectral cone turned its apex towards the distant end of the tube, and from its circular base filmy drapery seemed to fall. Placed on the base of the cone was an exquisite vase, from the interior of which sprung another vase of similar shape; over the edges of these vases fell the faintest clouds, resembling spectral sheets of liquid. From the centre of the upper vase a straight cord of cloud passed for some distance along the axis of the experimental tube, and at each side of this cord two involved and highly iridescent vortices were generated. The frontal portion of the cloud, which the cord penetrated, assumed in succession the forms of roses, tulips, and sunflowers. It also passed through the appearance of a series of beautifully shaped bottles placed one within the other. Once it presented the shape of a fish, with eyes, gills, and feelers. The light was suspended for several minutes, and the tube and its cloud permitted to remain undisturbed in darkness. On re-igniting the lamp, the cloud was seen apparently motionless within the tube; much of its colour had gone, but its beauty of form was unimpaired. Many of its parts were calculated to remind one of Gassiot's discharges; but in complexity and, indeed, in beauty, the discharges would not bear comparison with these arrangements of cloud. A friend to whom I showed the cloud likened it to one of those jelly-like marine organisms which a film barely capable of reflecting the light renders visible. Indeed no other comparison is so suitable; and not only did the perfect symmetry of the exterior suggest this idea, but the exquisite easing and folding of film within film suggested the internal economy of a highly complex organism. The twoness of the animal form was displayed throughout, and no coil, disk, or speck existed on one side of the axis of the tube that had not its exact counterpart at an equal distance on the other. I looked in wonder at this extraordinary production for nearly two hours *.

The precise conditions necessary to render the production of the effects observed with hydrobromic, hydrochloric, and hydriodic acids a certainty have not yet been determined. Air, moreover, is the only vehicle which has been employed here. I hazard no opinion as to the chemical nature of these reactions. The dry acids, moreover, I have not yet examined.

^{* &}quot;It is as perfect as if turned in a lathe." "It would prove exceedingly valuable to pattern-designers," were remarks made by my assistants as they watched the experiment. Mr. Ladd, who is intimately acquainted with the phenomena of the electric discharge through rarefied media, remarked that no effect he had ever seen could compete in point of beauty and complexity with the appearance here imperfectly described. I mention this to indicate how the phenomena affected other eyes than mine.